EVALUATION OF THE PERFORMANCE OF WAX INHIBITORS ON WAX DEPOSITION

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ABSTRACT

Chemical methods were implemented in the crude oil industry to reduce wax deposition in transportation of crude oil via pipeline in subsea conditions. Poly (ethylene-co-vinyl acetate) (EVA) and diethanolamine (DEA) were used in this study to evaluate the performance as an effective wax inhibitor pair at different blend volume ratios in crude oil using cold finger method equipped with an agitator. Aside from that, the study on the rheology behaviour was carried out to validate the effects temperature and shear on the viscosity of the untreated crude oil. 10 mL volume of the wax inhibitor was injected into the cold finger equipment operating at 200 rpm, cold finger temperature at 10 ˚C, and water bath temperature surrounding the vessel at 50 ˚C. It was found that at ratio 1:1 of EVA at 400 ppm concentration to DEA was proven to be the most effective ratio blend at this operating condition with paraffinic inhibition efficiency (PIE) of 50.26%. It was also shown that EVA alone performs far better than DEA with a PIE of 17.28%. However, blend of wax inhibitors outperforms pure wax inhibitors in reducing wax deposition by a significant margin of greater PIE. The wax deposited from the inhibition of pure EVA gives a relatively hard wax texture in comparison to inhibition of pure DEA which gives a relatively softer wax texture. Wax inhibitor blends between EVA and DEA on the other hand give the softest gel texture which implicates the wax to contain lower hydrocarbons. The rheology behaviour of the crude oil behaves close to a pseudo plastic fluid where the viscosity decreases with increasing shear rate and increasing temperature. The result here will be useful to understand the effectiveness of EVA in the presence of wax dispersant, DEA to prevent severe pipeline blockage and losses of crude oil production by controlling wax deposition. It is recommended for future researches to evaluate the performance of wax inhibitor blends by varying the parameters of the cold finger equipment with respect to factors attributing to wax deposition such as molecular diffusion, shear dispersion, and effects of aging.

ABSTRAK

Kaedah kimia telah diamalkan dalam industri petroleum untuk mengurangkan pemendapan wax dalam activity pengangkutan petroleum melalui saluran paip di dasar laut. Poly (ethylene-co-vinyl acetate) (EVA) dan diethanolamine (DEA) telah digunakan dalam kajian ini untuk menilai prestasi sebagai campuran perencat wax pada nisbah gabungan yang berbeza untuk mengawal isu pemendapan wax menggunakan alat '*cold finger'*. Selain daripada itu, kajian reologi dijalankan untuk mengesahkan kesan suhu dan ricih pada kelikatan minyak batu. 10 mL perencat wax telah disuntik ke dalam '*cold finger'* yang beroperasi pada 200 rpm, suhu jari sejuk pada 10 ˚C, dan air suhu mandi sekitar bekas minyak batu pada 50 ˚C. Daripada keputusan eksperimen ini, didapati bahawa pada nisbah 1:1 EVA-DEA merupakan gabungan nisbah yang paling berkesan dengan wax perencatan kecekapan (PIE) sebanyak 50.26%. Ia juga menunjukkan bahawa EVA berfungsi lebih berkesan sebagai perenncat wax daripada DEA dengan PIE daripada 17.28%. Walau bagaimanapun, campuran perencat wax didapati lebih berkesan daripada menggunakan perencat wax tanpa campuran dalam mengurangkan pemendapan wax. Wax daripada perencatan tulen EVA memberikan tekstur wax yang keras berbanding dengan perencatan tulen DEA yang memberikan tekstur wax yang lembut. Pergabungan perencat wax antara EVA dan DEA sebaliknya memberi gel tekstur paling lembut dalam eksperimen ini. Tekstur tersebut mengimplikasi wax tersebut mengandungi molekul hidrokarbon yang rendah. Reologi minyak batu didapati bersifat hampir cecair plastik pseudo di mana kelikatan berkurangan dengan peningkatan kadar ricih dan suhu. Hasil eskperimen ini adalah untuk penambahan latar belakang keberkesanan perencat wax hasil perganbungan EVA dan DEA. Ilmu ini akan digunakan untuk mengelakkan pemendapan saluran paip daripada tersumbat di dasar laut sehingga mengakibatkan kerugian produksi. Ia adalah dicadangkan untuk menyelidik pretasi perencat wax dengan mengubah parameter alat '*cold finger'* untuk mengaitkan faktor-faktor penyebab pemendapan wax seperti resapan molekul, pebaran ricih, dan kesan-kesan penuaan.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

m_m	mass of deposited wax
ρ_d	density of the solid wax
D_m	diffusion coefficient of liquid wax in oil
A	surface area over which deposition occurs
C	concentration of wax in solution
r	radial coordinate
T	temperature of the bulk fluid
W_f	reference amount of wax deposition without chemical treatment
W_t	amount of paraffin deposition with chemical treatment

LIST OF ABBREVIATIONS

API	American Petroleum Institute
ASTM	American Standard Testing Method
CCN	Carbon critical number
DEA	Diethanolamine
DSC	Differential scanning calorimeter
EVA	Poly (ethylene-co-vinyl acetate)
HMWH	High molecular weight hydrocarbons
LMWH	Low molecular weight hydrocarbons
PIE	Paraffinic inhibition efficiency
PPD	Pour point depressant
PPT	Pour point temperature
SARA	Saturates, asphaltenes, resins, and aromatics
UOP	Universal Oil Products
WAT	Wax appearance temperature
WDT	Wax disappearance temperature

1 INTRODUCTION

1.1 Background and motivation of study

Wax deposition in subsea pipelines is a complex phenomenon that has brought many challenges in the production, transportation and refining of crude oil in the petroleum industry. Wax deposition occurs due to the decrease in temperature and pressure during oil production operations which induces the precipitation wax crystals to form from crude oil and deposit onto pipeline walls. Crude oil is mainly composed of saturates, asphaltenes, resins, and aromatics (SARA). It was found that saturates also known as n-paraffins are the main culprit that contributes to wax deposition (Nanthan, 1955). The solubility of n-paraffins decreases with decreasing temperature and pressure leading to the formation of wax precipitates that has the potential to create crystalline net capable of entrapping liquid crude oil (Jorda, 1966). The temperature gradient between pipeline walls and the bulk fluid temperature driven by molecular diffusion mechanism will then cause wax deposition to occur on the surface of pipeline walls. Waxes that manage to deposit onto pipeline walls offer available nucleation sites that attracts other non-polar n-paraffins to bond layer upon layer of wax deposits. The built up wax deposits on pipeline walls would hinder transportation via pipeline operations by causing drastic increase of pressure drop in pipelines, reduction in diameter of the pipe or pipeline blockage resulting to major losses in profit and time to restart the production line (Wu *et al.*, 2012).

Chemical additives also known as wax inhibitors are one of the known wax controlling strategy being implemented by petroleum production industries to reduce the frequency of pigging. Wax inhibitors such as pour point depressants (PPD) and wax dispersants were used to chemically modify the wax solid structure thus reducing the tendency of the wax crystals to interlock and form three dimensional networks growth (Pederson & Rønningsen, 2003). These wax inhibitors are highly responsible in retarding the growth of the wax paraffin to form smaller crystals with higher volume-to-surface ratio. Wax inhibitors do not however, stop the precipitation from happening but creates a temporary kinetic barrier to precipitation that delays the precipitation mechanism from forming harden wax, allowing these wax aggregates to be swept away in the oil production stream flow in time (Tinsley *et al.*, 2009).

Although under the class of chemical additives, the role of PPD and wax dispersants differs widely from one another. PPD also known as wax crystal modifiers functions by co-crystalizing into the paraffin structure through van der Waals interactions leaving the polar moiety end tail to create a steric hindrance to interfere with alignment of new incoming wax molecules. Meanwhile wax dispersants functions by absorbing itself onto the wax crystals, preventing crystal nucleation phenomenon thereby reducing the tendency of the wax molecules to stick together. Frequently, wax dispersants are blended with wax inhibitors to enhance their performance in reducing wax deposition (Malcom, 2009; Marie *et al.*, 2004).

The motivation behind this research is to evaluate the performance of PPD blended with wax dispersant on wax deposition quantitatively and qualitatively. The wax inhibitor and wax dispersant selected for this study are poly (ethylene-co-vinyl acetate) (EVA) and diethanolamine (DEA) respectively. It is desired through the outcome of this research to expand the literature on the role wax inhibitor play in reducing wax deposition in terms of the amount of mass of the wax deposited and the effects it has on the hydrocarbons.

1.2 Problem statement

Wax deposition only requires the presence of wax precipitation as little as 2 wt. % (Létoffé *et al.*, 1995) and the driving force of molecular diffusion mechanism to occur. Malaysia oil wells were literately reported to contain as high as 20.2 wt. % of wax content and pour point temperature (PPT) as high as 36 ˚C (Kelechukwu & Yassin, 2008). With the world oil demand expecting to increase by 50% in 2025 (U.S. Department of Energy, 2004), offshore productions are expected to experience even colder subsea conditions of at least 5 ˚C with increasing offshore oil rigs distance (Azevedo & Teixeira, 2003). The transportation of crude oil via subsea pipelines will severely experience pipeline blockage due to heavy wax formation on pipeline walls leaving petroleum companies with an alarming economical viable issue due to frequent downtime and risk of damaged equipment forced to be abandoned. The percentage of offshore wells built in water depths greater than 500 m are expected to increase from 55% in 2007 to 67% in 2012 with the deepest well forecasted to be as deep as 3000 m below sea level (Wright, 2007). Currently, South China Sea, the Gulf of Mexico, North

Sea, off the coast of West Africa and off the coast of Brazil are amongst the most active offshore well productions to date (Azevedo & Teixeira, 2003).

Chemical methods typically used to address wax deposition issues are widely being studied due to their efficient role in reducing the frequency of costly pigging. Extensive studies were carried out on the role of PPD such as ethylene co-polymers, maleic anhydride co-polymers, and α-olefins co-polymers on the viscosity, pour point and efficiency of paraffin wax inhibition using laboratory methods such as cold finger method, flow loop method and rheometer to simulate the environment as similar as sub-sea pipeline (Machado & Lucas, 1999). The role of wax dispersants were typically studied by introducing novel chemicals created to control wax deposition. However, not much literature documentation was done on the effects on wax deposition through association of PPD with wax dispersants as most researchers are primarily focus on introducing novel chemicals primarily in the area of wax inhibitors. Even so, it is still generally understood that wax dispersants enhance the performance of wax inhibitors by reducing wax deposition by adhering pipeline wall and onto wax precipitates preventing aggregation between wax molecules.

1.3 Objective

The following is the objective of this research:

- To evaluate the effects of combined blend wax inhibitors EVA and DEA on the wax deposition in crude oil using cold finger method.

1.4 Scopes of this research

This experimental study is conducted using the cold finger method equipped with a stirrer to agitate the crude oil inside the vessel. The following are the scopes of this research:

i. Untreated crude oil samples will be characterised with respect to (i) wax appearance temperature (WAT) using Differential Scanning Calorimeter (DSC) (ii) determination of PPT using American Standard Testing Method (ASTM) D-97 (iii) viscosity temperature and rotational speed of spindle dependence using Brookfield viscometer (iv) amount of wax content using modified UOP46-64 method (Burger *et al*., 1981).

ii. Using cold finger method to determine the optimum ratio blend between a selected pair of wax dispersant with pour point depressant by evaluating the paraffinic inhibition efficiency (PIE) (Bello *et al.*, 2006) from the mass deposited onto the cold finger.

1.5 Significance of study

Wax deposition is an alarming phenomenon that has economically burden the transportation of crude oil in the oil and gas industry. The significance of this study is to expand the literature background on the influences of PPD enhanced by the presence of wax dispersants to resolve wax deposition in subsea pipelines in hopes that this knowledge would aid in lowering down the production cost of crude oil from offshore productions. Chemical methods are relatively economical to study and also apply in the oil production industry in comparison to other wax controlling strategies. Other viable methods are also possible but they can be costly such as hot oiling which consumes a lot of energy resulting to high cost of utilities.

As a result, the effect of the selected wax inhibitor pair on wax deposition is being evaluated using cold finger method to determine the optimum ratio blend with the highest PIE. From the result obtained, it is desired to expand the understanding on the role of wax dispersants and wax inhibitors. It is also desired to recommend wax deposition using cold finger method as a relatively cheaper alternative than the flow loop method to screen for potential PPD experimentally.

1.6 Organisation of this thesis

The structure of the remainder of the thesis is outlined as follow:

Chapter 2 provides a description of the mechanisms involved in wax deposition and the chemical methods studied in modern literature to resolve wax deposition issues. A general discussion of various laboratory methods other than the cold finger method was also presented. A summary of various cold finger method studies was also provided.

Chapter 3 gives a review on the cold finger methodology and the wax characterization of the crude oil. The wax characterization considered in this study involves determination of WAT using DSC, PPT using ASTM D-97 and amount of wax content

using modified UOP 46-64 method. The methodology of rheology behaviour of crude oil was also discussed.

Chapter 4 is devoted to the result and discussion obtained from the experimental study carried out. The wax characterization was done on untreated crude oil to obtain its physiochemical properties; WAT, PPT and amount of wax content. A brief discussion was done on the rheology behaviour of the untreated crude oil based on the viscosity readings collected from the rheology experiment. Aside from that, the results on the optimum ratio of the combined PPD and its effects on the wax deposited were discussed.

Chapter 5 concludes the results obtained from this research and provides future recommendations to improvise this study and provide suggestion on potential further studies that could carried out by other researchers interested in addressing wax deposition using chemical methods by performing experimental studies using cold finger method.

2 LITERATURE REVIEW

2.1 Overview

This chapter presents the past studies that have been performed on wax deposition from the thermodynamic and hydrodynamic view points and the efforts to experimentally predict wax deposition. The molecular diffusion, shear dispersion and aging effect are of the many significant factors that lead to wax deposition. The roles of these factors on wax deposition were also discussed in detailed such as the effect of a large differential temperature, shear stripping effect and the effects of flow regime on wax aging (Jessen & Howell, 1958; Jorda, 1966; Azevedo & Teixeira, 2003; Singh *et al*., 2001). Aside from that, this paper also covers on the development of EVA as a commercial PPD and DEA as a wax dispersant and their aspects as part of the waxy crude oil treatment. In addition, the cold finger method is also explained as an introductory literature and also other possible methods of performing laboratory scale wax deposition related experiments.

2.2 Introduction

Wax deposition is amongst the several critical operational challenges faced by the production and transportation pipelines in deepwater oil and gas industries. The pipeline acts as an intermediate form of transportation between the reservoir field to oil rig platform and oil rig platform to onshore upstream refinery plants. In order to prevent major loss of crude oil production due to blockage of these pipelines, strong pumping power and frequent pigging; a mechanical treatment to remove deposited wax on pipeline walls is required. However the increase in distance and depth of subsea transportation via pipeline has increase the frequency of pigging and risk of clogged pipes, which in turn creates an economical issue to the crude oil production team.

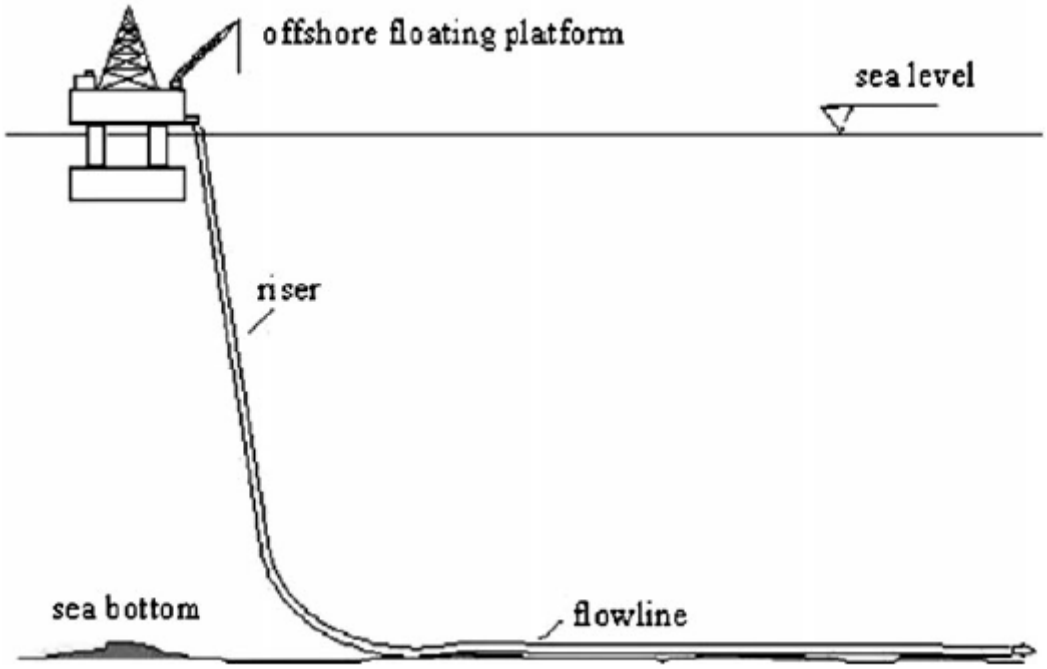

Figure 2- 1: Illustration of a subsea flow line from oil rig platform to upstream refinery plant by Gooya *et al.*, (2013).

The solubility of paraffin in crude oil is highly dependent on the decreasing function of temperature, pressure and the molecular weight of its constituents. As the crude oil leaves the reservoir, the pressure and the temperature of the bulk fluid tends to decrease in the process of its production and transportation. When crude oil at reservoir temperature is loss to surrounding pipeline walls in subsea climate, it tends to form wax precipitates that interlocks into a three dimensional network. Oil is entrapped in this network and forms gel-like structure below WAT. Further cooling subjects to the gel to harden and clog pipelines (Hemant *et al.*, 2008).

Crude oil constituents consist of n-alkanes, asphaltenes, resins, lighter distillates methane hydrates, polar aromatics, nitrogen, and sulphur etc. It is believed that long, straight n-paraffin chains are pre-dominantly responsible for the formation of wax deposits; even in most of Malaysian crude oil fields (Kelechukwu & Yassin, 2008). Nevertheless, not all long-chain aliphatic alkane compounds (C_nH_{2n+2}) exhibit the tendency to form wax deposits.

Table 2-1: Past studies regarding the nature of the deposited wax from crude oil.

Description	Reference
High molecular weight hydrocarbons (HMWH) that predominantly fall in the range of C_{18} to C_{65}.	Srivastava *et al.* (1993)
Present of aromatics, paraffin (C_{18} to C_{36}) and naphthalene components (C_{30} to C_{60}).	Bai and Bai (2010)
Paraffin exist in three forms: 1. Macrocrystalline: Dominated by straight chained n-alkanes found in subsea and export pipelines 2. Semi-microcrystalline: Intermediate between macro- and microcrystalline paraffin. 3. Microcrystalline: Often cycloalkanes and branched alkanes often associated with asphaltenes and other solid deposits found in tank bottoms as sludge-like deposit.	Wylde (2012)
Wax structures depends on the wax concentration, crystallization habit of wax, and the shear stability	Holder and Winkler (1965)

2.2.1 The differences between wax precipitation and wax deposition

Crude oil typically flows out of the reservoir at 70-150 °C and 55-103 MPa into subsea pipelines (Singh *et al.*, 2001). At elevated water depths, the relative constant ambient sea bed temperatures can range from 4 to 8 °C (Rønningsen, 2012). Below WAT, crude oil may separate into a solid-liquid wax phase where wax precipitation is first observed. Wax precipitation has the ability to form three dimensional structures due to the agglomeration of orthorhombic wax crystals nucleation sites (Paso & Folger, 2004). It is thermodynamically driven by variables such as temperature, pressure and composition; hydrodynamically influenced by flow regime; heat and mass transfer; solid-solid and surface solid interactions (Hammami *et al*., 2003). These wax crystals tend to increase the viscosity of crude oil resulting to higher drag force.

However, the difference between wax precipitation and wax deposition lies here. It is necessary for wax precipitation to occur first before wax deposition can happen. Thus, it is also possible for wax precipitation to happen without leading to wax deposition. Though, it only requires at least 2 wt. % of precipitated wax to cause gelling of virgin waxy crudes (Li *et al*., 2005; Holder & Winkler, 1965; Létoffé *et al.*, 1995). With the aid of the surface roughness on the pipeline walls at a certain flow regime and lower

pipe wall temperature, these precipitates would get entrapped onto the pipeline walls as wax deposits and slowly thicken with time (Patton *et al*., 1970).

2.3 Wax appearance temperature and wax disappearance temperature

WAT is the temperature at which the wax crystals begins to form and precipitate gradually from the solution. The method of WAT determination is influenced by the supercooling involved in the crystallization process. A crude oil with higher composition of light end hydrocarbons tends to have lower WAT. This is due to the presence of light ends acting as a solvent to stabilize the higher end of the hydrocarbons in the crude oil. Reducing pressure further however would cause the lighter molecule weight hydrocarbons to dissipate as gas phase from the crude oil. This effect reduces the solubility of HMWH, thus increasing the WAT of the bulk fluid. Higher WAT would result to wax precipitation at elevated temperatures. This is problematic to subsea pipeline as even relatively warm climates water temperature tends to be around 5 °C (Azevedo & Teixeia, 2003).

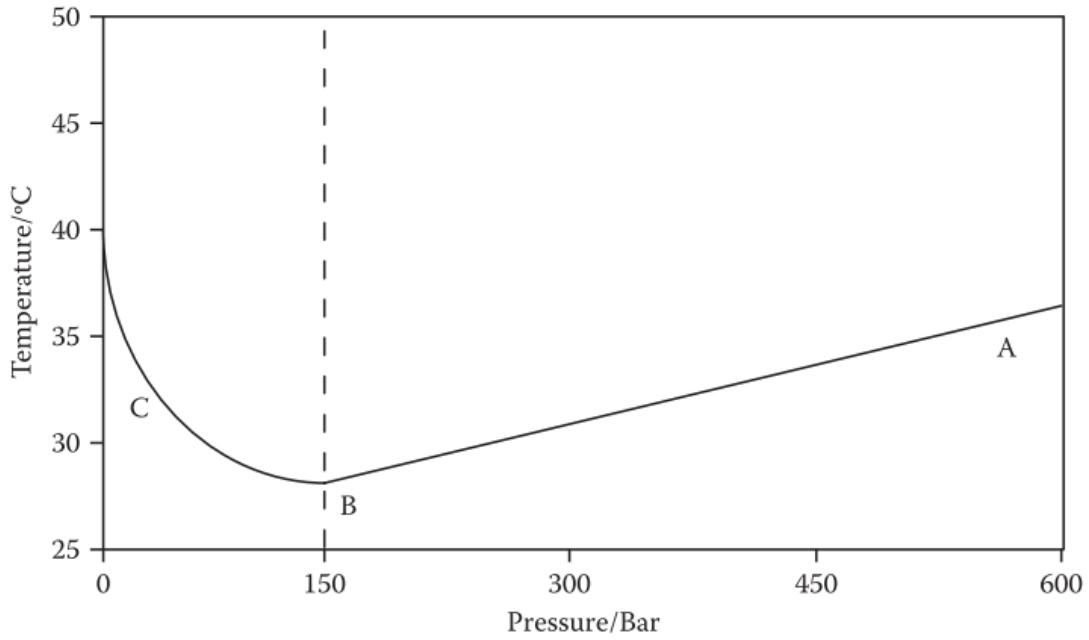

Figure 2- 2: Illustration of a typical phase diagram for wax precipitation by Malcolm (2009, p. 262).

According to Malcolm (2009), in Figure 2-2 point A represents the point at which the crude oil is undersaturated at reservoir pressure. As fluid is produced, the pressure falls and the lighter molecular weight hydrocarbons expand in greater proportion to the

dissolved waxes. At point B, the ratio the volume of the light ends to heavy ends is at its greatest. However further reduction of pressure would result to increase in WAT. The curve in point C, reflects the effect of further decreasing pressure which disintegrates the lighter ends of the hydrocarbons thus increasing the WAT of the crude oil.

When the crude oil temperature starts to precipitate in descending rank order according to molecular weight due to super saturation, a single liquid phase of the oil changes into solid-liquid dispersion system at which small amount of wax crystals becomes present in liquid phase. If this system were to be heated at WAT, these wax crystals will still remain present and requires a higher temperature to dissolve them. This temperature is termed as wax disappearance temperature (WDT). WDT which Bhat and Mehrotra (2004) found to be close to the thermodynamic liquidus temperature is believed to be the true solid-liquid phase boundary. It is found WDT to be on an average of 3 °C higher than WAT for prepared wax-solvent mixture consisting C_{20}-C_{40} (Bhat & Mehrotra, 2004).

The difference in WAT and WDT is crucial when trying to determine the cloud point, pour point, and rheology behaviour of the crude oil. Shear and thermal history is normally eliminated by heating the crude oil for a few hours. This is further discussed under Chapter 3 as it concerns the determination method cloud point, pour point, cold finger experiment and determination of the rheology behaviour carried out.

2.3.1 Cloud point and pour point correlation

Cloud point represents the solubility limit of crude oil where solid wax crystals first precipitate. It is also known as WAT. On other hand, PPT is the lowest temperature at which crude oil will flow or pour. It is also greatly affected by oil flow properties. It results to dramatic changes in the viscosity and flow properties of crystallization of paraffin crystals. It can be modified using chemical inhibition method which lowers its pour point.

2.3.2 Rheology behaviour of crude oil

Crude oil at high temperature behaves as a Newtonian fluid showing viscosity-temperature dependence. As the temperature of the crude oil falls below the WAT, precipitation of the wax crystals will suddenly rapidly increase the viscosity entering into the non-Newtonian fluid region. The yield stress of a wax-solvent mixture is

believed to be a function of wax composition, and thermal and shear histories. A typical waxy crude oil would normally exhibit a pseudo-plastic with thixotropic properties (Matveeko *et al*., 1995).

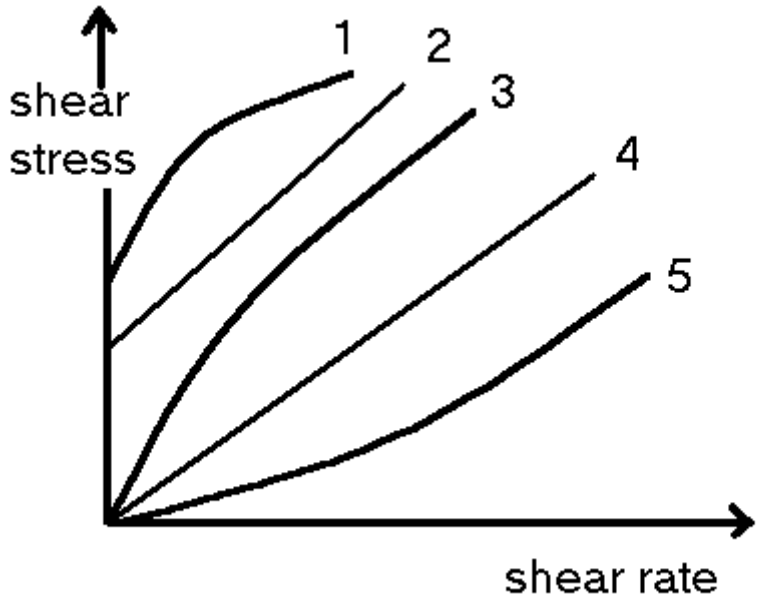

Figure 2- 3: Summary of non-Newtonian fluids (1) Viscoplastic fluid (2) Bingham fluid (3) Pseudo plastic fluid (4) Newtonian fluid (5) Dilatant fluid

The untreated crude oil is found to behave similarly to pseudo plastic fluid. Where with increasing shear rate, the viscosity tends to decrease. This behaviour is termed as shear-thinning.

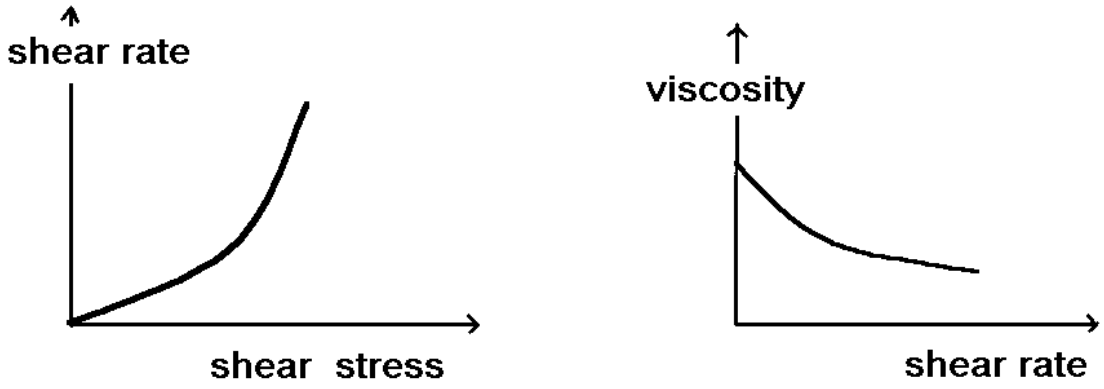

Figure 2- 4: The nature of a pseudo plastic fluid

According to Cheng *et al*. (2000) the nature that untreated crude oil exhibits a non-Newtonian behaviour can described in Bingham style equation. The deviation of the peak from linearity shows an elastic response, followed by creep and the final fracture.

2.4 Wax deposition mechanism

Various investigations have been carried out for the past decades on wax deposition mechanism by several researchers (Burger *et al*., 1981; Leiroz & Azevedo, 2005). Different methods have been suggested by different researchers and found to play a significant role in wax deposition. The molecular diffusion and shear dispersion mechanism are found to likely be the primary driving force of wax deposition amongst the mechanisms that have been proposed (Malcolm, 2009).

2.4.1 Molecular diffusion mechanism

Simply said, molecular diffusion occurs if the pipe wall is colder than the WAT, wax can form and deposit onto the wall due to the temperature gradient existing between the pipe walls and the bulk fluid which is driven by Fick's law.

$$\frac{dm_m}{dt} = \rho_d D_m A \frac{dC}{dr} = \rho_w D_m A \left(\frac{dC}{dT}\right)\left(\frac{dT}{dr}\right) \tag{2.1}$$

In equation 2.1, m_m is mass of deposited wax, ρ_d is the density of the solid wax, D_m is the diffusion coefficient of liquid wax in oil, A is surface area over which deposition occurs, C is the concentration of wax in solution, T is the temperature of the bulk fluid, and r is the radial coordinate

Large temperature differential will lead to greater wax deposition with a weak porous structure (Jessen & Howell, 1958; Jorda, 1966). The initial wax deposition will increase rapidly and then the rate of deposition will decrease again due to the insulating effect of the wax layer (Towler *et al*., 2011).

2.4.2 Shear dispersion mechanism

Shear dispersion occurs when already precipitated wax close to the wall moves to a region of lower velocity in the pipe wall and deposits (Malcolm, 2009). This mechanism is shown to have no effect to deposition in the absence of heat flux despite the bulk fluid temperature being under cloud point conditions (Burger *et al.*, 1981; Azevedo & Teixeira, 2003). Despite this, the drag force exerted on the solid waxy crystals from the fluid contributes to the removal of wax and aging of wax deposits which is known as

the shear stripping effect. Thus, flow regime within the subsea pipeline also plays a major role in wax deposition. Laminar flow and turbulent flow are currently the two main most fully understood flows that play an influential role on wax deposition.

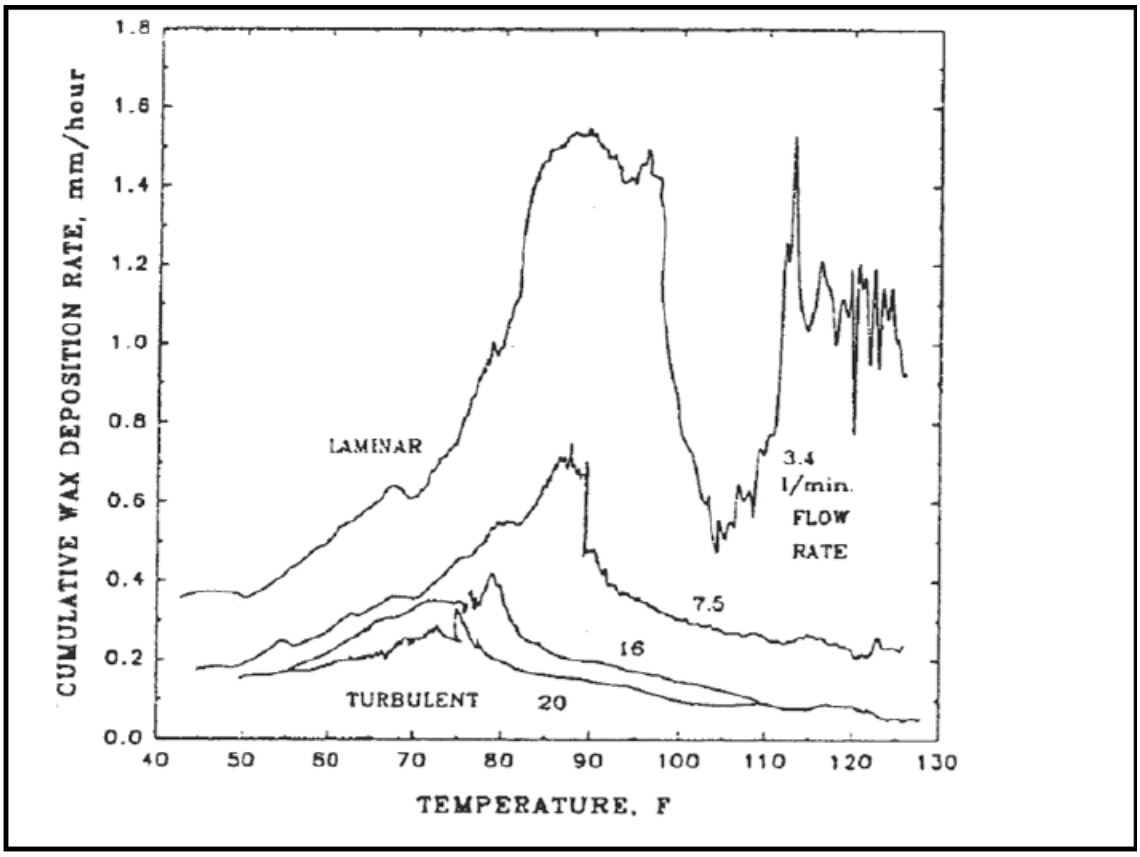

Figure 2- 5: Effect of flow rate on wax deposition rate by Hsu *et al*. (1994).

The laminar flow of the bulk fluid allows longer residence time of the crude oil to lose heat to surrounding colder pipeline walls (Towler *et al*., 2011). This allows the wax molecules to easily stick onto pipe walls and cluster together. Turbulent flow regime, on the other hand tends to reduce the wax deposition from occurring as it disrupts the adhering and growing of wax deposits. However, mostly wax crystals in this flow regime tend to be hard in nature and capable of depositing on pipeline walls (Towler *et al*., 2011).

2.4.4 Other proposed mechanisms

Other deposition mechanisms have been proposed as well but are not found to have a major significant effect on wax deposition. Such is the Brownian diffusion mechanism. It also encompasses the Fick's Law where by, the precipitated wax crystals would collide with other thermally agitated oil molecules. Another mechanism called the

gravity settling where gravity influences wax deposition due to the density difference between precipitated waxy crystals and oil phase. However, Burger *et al*. (1981) have showed that settling velocities of wax crystals under typical conditions do not contribute significantly to deposition. This was supported with experimental evidence which shows that deposition under horizontal and vertical flow is identical within the limits of experimental error. The contribution of gravity deposition and Brownian diffusion is typically negligible for most research cases at the moment (Correra *et al.*, 2006; Kjøraas, 2012, p. 7)

2.4.5 Wax aging

The gel hardening phenomenon is known as aging. A gel behaves as a porous medium in which wax molecules continue to diffuse through due to radial variation in temperature. This effect is due to the counter diffusion of n-paraffin molecules having a carbon number lower than the critical carbon number (CCN) outer gel layer. Thus, light n-paraffin components diffuse from liquid phase of the gel deposit to the bulk oil, while the heavy n-paraffin components diffusion from the bulk oil into the gel deposit. The wax content of the deposited gel increases with time (Paso & Folger, 2003; Singh *et al.*, 2000).

It was found that wax content to be a strong function of aging time and temperature difference across it. This was validated through a flow loop experimental data (Singh *et al*., 2000). Oddly it was also found that an increase in the wall temperature or flow rate results in a decrease in the gel thickness and consequently an increase in the rate of wax content aging of the gel.

2.5 Chemical methods

It is understood that wax inhibitors have certain combination of mechanisms involving nucleation, co-crystallization and adsorption which contributes to the process of wax crystallization (Behbahani *et al.,* 2011). Though, the deviations from expected crystallization can be easily influence the presence of other components such as aromatics, asphaltenes, resins, water, additives, modifiers, PPDs and shorter-chained n-paraffins. This deviation particularly interests us as the change in wax morphology affects the cloud point, pour point, fluid viscosity, fluid rheology behaviour, and gel strength of the wax crystals. Over the years, extensively used wax modifiers that were

studied can be summarized as the following: highly branched poly-α-olefins, ethylene-vinyl copolymers, alkyl esters of unsaturated carboxylic acid-α-olefin copolymers, ethylene-vinyl fatty acid ester copolymers, long-chain fatty acid amides and poly n-alkyl acrylates and methacrylate copolymers (Machado & Lucas, 2002).

Basically, there are three groups of chemicals used to resolve wax deposition issues which are wax crystal modifier, detergents and dispersants. A molecular structure of a wax crystal modifier consists of a hydrophobic chain that interacts with the paraffin molecules and a polar moiety which is responsible for modifying the wax crystals morphology (Machado *et al.*, 2001). They are capable of altering the growth and surface characteristics of the crystals thereby reducing the tendency of the crystals to stick to metal surfaces such as pipe walls and lowering pour point and viscosity (Pederson and Rønningsen, 2003). There are many different observations reported on the performance of these wax inhibitors such as large or small crystals form, aggregate structures, and the presence of asphaltenes hindering the ability of the PPD to perform its aggregation (Tinsley *et al.*, 2009). Malcolm (2009) classified PPDs into ethylene polymers and copolymers, comb polymers, and miscellaneous branched polymers with long alkyl groups. These classes of polymer have slightly different characteristics of inhibiting the wax but they similarly function to aggregate and modify the crystal structure. It is important to keep in mind that PPDs are formulated into products with active polymers contained in a solvent. The amount of polymer that can dissolve in a solution is still dependent on the thermodynamic phase behaviour of the polymer solution such as the temperature and pressure effect. Wax modifiers do not however, stop the precipitation from happening but creates a temporary kinetic barrier to precipitation that delays the precipitation mechanism from forming irreversible harden wax, allowing these wax aggregates to be swept away in the oil production stream flow in time (Tinsley *et al.*, 2009).

Detergents and dispersants on the other hand, are surface-active agents known as surfactants that keep the wax crystals dispersed to reduce the interaction between the solid surfaces. Surfactants also known as wetting agents can be classified into cationic, anionic and non-ionic surfactants. Despite having similarity in chemical structure with PPD, wax dispersants are known to have higher polar functional group that defines its surfactant character (El-Gamal, Khidr & Ghuiba, 1998). Not much studies has been carried out to define the role of wax dispersants on wax crystals but it is generally